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STUDY OF STRUCTURE INFLUENCE ON WEAR RESISTANCE OF HIERARCHIAL SUPERHYDROPHOBIC COATINGS

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Досліджено взаємозв'язок між конфігурацією ієрархічних структур поверхні супергідрофобних покриттів і їх стійкістю до абразивного зносу. Встановлено вплив вмісту фракцій мікророзмірних наповнювачів, а також матричного полімеру на зміну кута скочування води з поверхонь. Вивчено механізм руйнування покриттів при абразивному зносі. Запропоновано шляхи отримання масштабованих зносостійких супергідрофобних покриттів з одностадійним нанесенням

Ключові слова: супергідрофобність, ієрархічна структура, кут скочування, механічна стійкість супергідрофобних покриттів

Исследована взаимосвязь между конфигурацией иерархических структур поверхности супергидрофобных покрытий и их устойчивостью к абразивному износу. Установлено влияние содержания фракций микроразмерных наполнителей, а также матричного полимера на изменение угла скатывания воды с поверхностей. Изучен механизм разрушения покрытий при абразивном износе. Предложены пути получения масштабируемых износостойких супергидрофобных покрытий с одностадийным нанесением

Ключевые слова: супергидрофобность, иерархическая структура, угол скатывания, механическая устойчивость супергидрофобных покрытий

1. Introduction

Materials are called superhydrophobic if they demonstrate the “lotus effect”. These materials feature three properties: (1) a drop of water forms a wetting angle of more than 150°; (2) the angle of rolling down, that is the angle of surface inclination to horizon at which a 2–3 mm drop begins to slide does not exceed 10°; (3) self-cleaning effect of the surface upon contact with water drops [1].

Studies have been conducted since the 1930s. During the last 15 years, superhydrophobic materials have become the subject of close attention of researchers due to a huge number of their possible applications. They can be used in construction in highly polluted cities due to the fact that such surfaces have self-cleaning properties. They also minimize the destructive environmental effect, do not allow water to enter microcracks and prevent icing. In addition, they can be used as filters for cleaning fuel and oils from water admixtures. Another important application is corrosion control [2].

Since then, knowledge of mechanisms of action of superhydrophobic coatings has made it possible to develop a number of methods of obtaining coatings with superhydrophobic properties on various surfaces. Such methods can include: application of coatings by means of templates, lithography, chemical and plasma etching, anodic oxidation, hydrothermal reactions, sol gel methods, electrospinning, layer-by-layer assembly, electrochemical deposition, chemical vapor deposition [3].

However, these methods are often expensive and can only be implemented within the laboratory, so they are not suitable for large-scale solutions. For this reason, this paper uses the method of traditional one-stage technology and environmental curing.

The relevance of this work is that one-stage methods for obtaining hierarchical superhydrophobic structures have not been adequately studied and the mechanism of abrasive destruction of such coatings is not known although this information is very useful for better design of such systems in future. Besides, thanks to a simple scaling process, they can be widely used in everyday life.

2. Literature review and problem statement

The wide application field of superhydrophobic coatings is hampered by their two main problems. The first problem is high price and complex hardware for the process of obtaining coatings, which does not allow scaling them to a proper extent. The second problem is mechanical instability of coatings, which lose their properties under intense abrasive action [4].

The problem of strength is solved quite effectively for yarns and fibers. For example, the use of silicone elastomer modified with hydrophobic silica nanoparticles and fluorinated with alkylsilane shows a good result in mechanical strength [5]. In addition, paper [6] shows how strength characteristics of the coating were significantly increased by incorporating polyaniline and fluorinated alkylsilane into cotton fabric. In such works, authors managed to obtain not only a mechanically resistant coating but also a coating resistant to acids and temperature. However, strong hydrophobic coatings for flat surfaces are still poorly investigated and no effective solution has been found yet.

In the last few years, various ways of solving these problems have been proposed:

– epoxy coating deposited by rapid evaporation [7];

– coating based on modified nanoparticles of hydrophobic silica [8];

– coating based on benzoxazine and mesoporous SiO_2 [9].

They have shown good strength characteristics in knife scratch control, sandpaper abrasion test and ASTM hardness test. These methods can be attributed to tangential wear resistance and they have been widely spread for testing superhydrophobic coatings. These tests fairly closely simulate the effects that the coating may encounter during their use. The problem with these methods is that there are many factors that depend on the experiments, on which the result depends itself, and it is often problematic to repeat them from experiment to experiment. They include pressure acting per unit area, contact area, abrasive movement speed. To avoid this problem, it is recommended to use the method of dynamic impact strength [4], namely the action of solid particles. This method simulates conditions of using the coating in outdoor applications. The number of factors influencing the result was minimized due to reduction of human participation in tests [4]. This method was used in a number works. For example, compositions based on acrylic polymer filled with nanoparticles of calcium carbonate were applied with brush in work [10]. Next, sand with a particle size of 200 μm was poured for 5 minutes and the nanocomposite was characterized by its water wetting angle. It remained hydrophobic after the test. Also, a superhydrophobic and simultaneously oleophobic surface was obtained in work [11] using soot which is formed in candle burning and siliceous shells. After that, soot was tested by the particle collision method but cracks began to form on the surface because of mechanical instability. Nevertheless, the surface retained superhydrophobic properties until the coating layer was completely removed.

The mechanism of microrelief scouring is not known up to now. It is assumed that the use of a composition based on particles of different dispersity will make it possible to obtain durable, wear-resistant superhydrophobic coatings.

3. The aim and objectives of the study

The objective of present work was to establish relationship between the fractional composition of fillers for superhydrophobic materials (the structure of the corresponding coatings) and stability of their characteristics under abrasive wear.

To achieve this goal, the following tasks were formulated:

– determination of the critical matrix content in three-fraction composites and elucidation of the effect of matrix content on hydrophobicity of coatings;

– structure study of hierarchical systems in composition of superhydrophobic coatings;

– determination of the relationship between abrasion resistance and fractional composition of the filler phase;

– study of the mechanism of scouring of the film layer of superhydrophobic coatings under wear.

4. Materials and methods for studying superhydrophobic surfaces

4. 1. Materials, equipment and preparation of coatings

The compositions were prepared using NeoCryl B-880, DSM NeoResins (The Netherlands) film-forming poly (styrene-butyl) methacrylates (SBM) in the medium of Sigma-Aldrich (USA) o-xylene. Ground Normcal-2 and Normcal-100 (Turkey) calcites were used as microfillers. Colloidal silica modified with AEROSIL R972 dimethyldichlorosilane, Resource Efficiency Evonik GmbH (Germany) was used as a nano-sized filler. All coatings were applied by pouring onto a glass surface and then drying at 50 °C to remove solvent.

Stearic acid was purchased from Sigma-Aldrich (USA). Propyl sodium silicate was obtained from Evonik Resource Efficiency GmbH (Germany).

Geometric and dimensional parameters of the fillers were obtained with the help of scanning electron microscopy (SEM) using REM-106 microscope (SELMI, Ukraine).

The values of the water wetting angle and the angle of water rolling in 5 ml of distilled water were measured using Goniomat M digital goniometer, Möller-Wedel GmbH (Germany). To analyze the morphology of water drops on surface, Delta Optical HCDE-50 camera (China) and corresponding ScopeTek View (China) software were used.

The filler surface treatment was as follows: ground Normcal-2 calcite (100 g) was treated with 114 ml of a 0.6 % by weight solution of stearic acid in o-xylene. A mixture of stearic acid and crushed calcite in o-xylene was left for 2 hours, followed by complete solvent evaporation at 80 °C. Normcal-100 was treated with 114 ml of 0.3 % by weight solution of stearic acid in o-xylene.

4. 2. The experiment procedure

Wear resistance test with hard particles. The tested coating was tilted at 45° to prevent re-deposit of particles after impact. Sand was poured at a constant rate from a container placed at a prescribed height above the surface. In this work, the height was 30 cm, and the particle diameter was 100–300 μm. After pouring 50 g of silica, the rolling angle was measured. The roll angle was tested until it fell to 90° and it was considered that the surface was completely scored off.

5. Results of the determination of the relationship between the structure of hierarchical superhydrophobic coatings and their resistance to abrasive wear

Characteristics of the initial dispersed fillers and their mass ratios to the polymer matrix (PMC) were determined at which the maximum stable value of the water wetting angle (mWA) was achieved (Table 1).

The fillers used in the work differed significantly in the degree of surface development: the maximum was for Aerosil R972, Normcal-2 surface was two orders lower, and Normcal-100 was three orders lower. This, in turn, caused difference in the values of critical concentration, which was minimal for Aerosil R972 and maximal for Normcal-100. The mWA values decreased with an increase in average particle size of the materials.

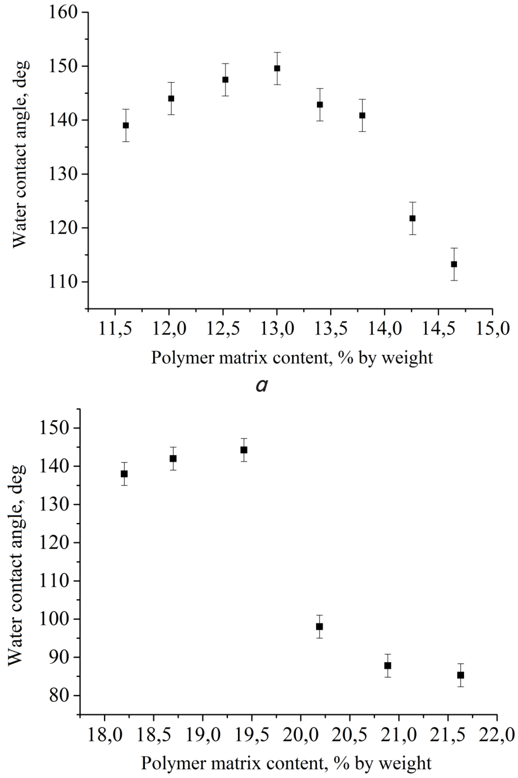
A three-level hierarchical structure of composition was used in this work. Microfillers play the role of a mechanically stable framework and the nanosized filler plays the role of a surface structuring agent. Critical concentrations of filler fractions in the acrylate matrix were determined for this system (Fig. 1).

Table 1

Characteristics of fillers

Filler	Average particle size d50 %, μm	Unit surface (BET), m^2/g	PMC, wt. %	mWA, grades	Density, g/cm^3	Volume density, g/cm^3
Aerosil R972	18.0×10^{-3}	115.03	48	162	2.35	0.35
Normcal-2	2.4	1.05	94	116	2.67	2.06
Normcal-100	26.5	0.11	96	108	2.70	1.95

As can be seen from Fig. 1, *a*, critical concentration of the acrylic matrix was achieved at its content of 13 wt. % under the condition of the indicated distribution of the filler fractions. As the content of the nanodispersed fraction increased (Fig. 1, *b*) from 5.3 to 15 % by weight, critical concentration of the polymer rose to 19.5 % by weight. Attention was drawn to the fact that as the content of the nanosized filler increased, the expected increase in the maximum wetting angle did not occur. For the first system, it was 149° and 144° for the second system.



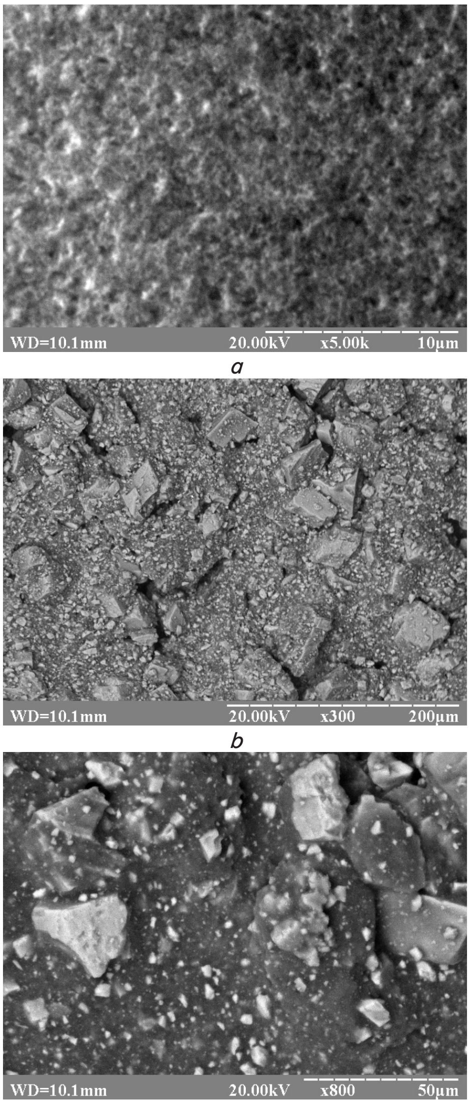
a

b

Fig. 1. Dependence between water contact angle of the composite film and concentration of the acrylic matrix: *a* — filled with Aerosil R972, Normcal-2 and Normcal-100 at weight ratio of 5.3: 31.6: 63.2, respectively; *b* — filled with the same system, but at the weight ratio 15:26:59

To determine influence of the fractional composition of fillers on the wear resistance of coatings, a number of compositions were prepared (Table 2). The composition was varied in terms of content parameters of nanosized and microfine fillers at two and three levels, respectively.

The surface structure of the coatings, which were obtained differed in size and configuration of irregularities (Fig. 2). E. g., a coating containing only one fraction (Aerosil R972, Fig. 2, *a*) was characterized by a fairly uniform relief formed by aggregate elevations of 0.3–0.4 μm particles; the three-fraction composition K1 (Fig. 2, *b*) had three types of elevations. Since microfillers do not practically aggregate, the height of these elevations was equivalent to the size of the corresponding particles. It should be noted that both the particles of the nanoscale fraction and the particles of the fine microsize fraction in the three-fraction systems covered the coarse-grained particles (Fig. 2, *c*) which created additional relief elements.



a

b

c

Fig. 2. Surface structure of composite films: *a* — two-component system of Neocryl 880 B and Aerosil R972, 52:48 % by weight, *b* — respectively; K1 composition; *c* — K2 composition

As can be seen from Fig. 3, nature of change in the rolling angle for coatings was the same in all cases. The curve beginning (the first section) was characterized by a steep increase in this index, after which the curve changed to a peculiar plateau (the second section) and there was a rapid index increase in the third section. Resistance to abrasion was numerically considered further as a coordinate of transition of the second section to the third one.

Table 2

Fractional composition of experimental coatings

Composition number	Filler content, % by weight			Polymer matrix content, % by weight
	Aerosil R972	Normcal-2	Normcal-100	
K1	4.6	27.6	55.2	12.52
K2	13.8	23.9	54.3	21.80
K3	13.8	13.8	64.5	21.80
K4	13.8	64.5	13.8	21.80
K5	13.8	0	78.3	19.70
K6	13.8	78.3	0	19.70

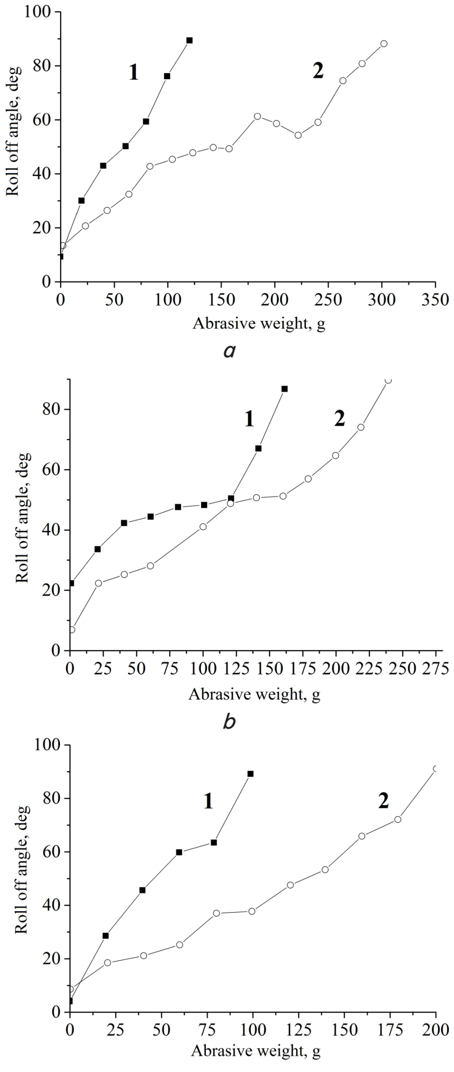


Fig. 3. Wear resistance of film composites: *a* — (1 — K1; 2 — K2); *b* — (1 — K4; 2 — K3); *c* — (1 — K6; 2 — K5)

It was found that increase in the content of nanosized filler from 4.6 to 13.8 % by weight (Fig. 3, *a*) resulted in increase in coating resistance to abrasion almost sixfold (from 60 to 240 grams). When the Normcal-2 content was increased to 64 % by weight, stability was reduced to 125 g (Fig. 3, *b*) and up to 170 g with an increase in the content of coarse filler to 64 % by weight. A complete exception of both fine (Fig. 3, *c*) and coarse fractions from the formulation exerts a more strong effect on wear resistance. At the same time, abrasion resistance decreased to 160 and 75 grams, respectively.

In general, the result shows that there is a certain optimum ratio of content of coarse and fine fractions, which is close to 2:1, respectively. At the same time, the system is more sensitive to the change in the content of coarse fraction, which indicates its decisive role in the formation of a mechanically stable relief.

The destruction kinetics of compositions under wear was studied using composition K2 as an example (Fig. 4). The initial composition (Fig. 4, *a*) had a uniform relief. At the beginning of wear (abrasive in amount of 150 g), 2–8 μm wide cracks appeared on its surface (Fig. 4, *b*). An increase in amount of abrasive (up to 300 and 400 g) led to the growth of these cracks (Fig. 4, *c, d*) to a width of 16-25 μm. Next, discrete flakes formed from the coating elements.

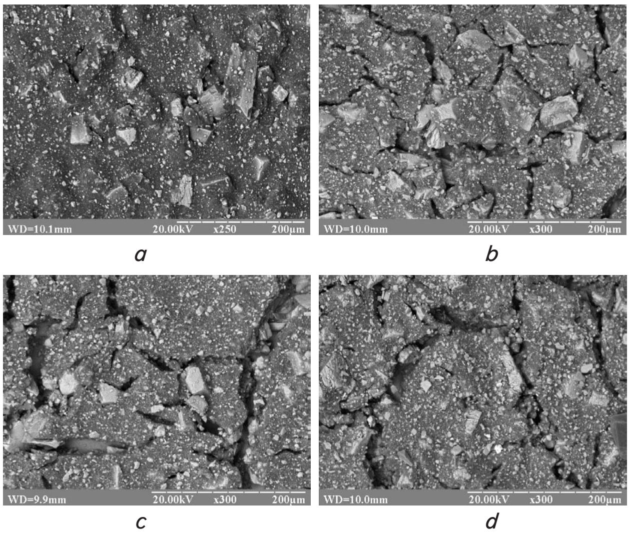


Fig. 4. Kinetics of coatings wear: *a* — initial composition of K2; *b* — K2 after a 150 g stream of abrasive particles; *c* — K2 after a 300 g stream of abrasive particles; *d* — surface of K2 after a 400 g stream of abrasive particles

It should be noted that there was a two-stage destruction of the relief of hierarchical structures of this type. At the first stage, which corresponds to the initial section of the attrition curve (Fig. 3), nanoscale fraction was carried over from the surface. This corresponds to a rapid (2–3 times) increase in the angle of rolling down from the original value. The second stage was much longer and consisted in a formation and growth of cracks in the polymer matrix. Ultimately, it led to the carry-over of macro-size surface elements and, consequently, to a sudden increase in the angle of the composition rolling down.

6. Discussion of the relationship between the structure of hierarchical superhydrophobic coatings and their resistance to abrasive wear

In determining wear resistance of hierarchical superhydrophobic compositions, it was found that the use of a combination of fractions makes it possible to increase 1.7–2.0 times (Fig. 3) service life of such coatings under abrasive conditions. The change in the fractional composition from the optimal ratio (for the selected fractions of the Normcal-2 and Normcal-100 microfillers, it was 1:2 by weight, respectively) led to a rapid increase in the rolling down angle index in all cases. It can be assumed that this effect was due to formation of a dense packing of filler particles on the surface of the coating which was achieved by using bifractional systems [12]. Under these conditions, the fraction of fine particles occupies a free volume of the coarse-particle fraction packing thus ensuring a more dense location of the irregularities on the surface (Fig. 2, *b*). The ratio of the average sizes of particles in microfractions approaches was 10:1 which is slightly higher than the optimal theoretical ratio [13].

It was established that the coarse fraction plays a decisive role in formation of stable superhydrophobicity of the systems under consideration (Fig. 3, *b, c*). In the case when it was replaced with a fine fraction, abrasion resistance of the coatings sharply decreased (up to 3 times at full replacement and up to 1.7 times at a 50 % replacement). The coarse fraction serves as a kind of shield for the surface against macroscopic bodies contacting with the coating. This role of the micro-sized part of the hierarchical structure was studied in [14, 15] but the degree of its influence on the final properties of the coating was not established.

The method for assessing wear resistance of coatings used to characterize them in the work has several advantages over the methods used to characterize such objects [16]. In particular, the nature of action of abrasive particles on the surface is close to the real situation of abrasive action. Particles do not move over the surface as a solid body but are in an individual contact with separate surface parts. Due to the standardized procedure, the results of this study method are more reproducible than, for example, the tests using sheet abrasives [17].

It was shown that the character of abrasive deterioration of the coating layer is of a two-stage nature. At the initial stage, the nano-sized fraction of the hierarchical structure is removed from the surface (Fig. 2) which is accompanied by a sudden increase in the angle of rolling down because of loss of the structure of corresponding level by the surfaces of micro-sized projections. In turn, this leads to the impossibility of forming the Cassie state in these areas and practically to formation of areas with a high wetting hysteresis. The further stage of destruction consists in the gradual growth of the cracks grids in the coating structure and a slight entrainment of elements of the micro-size structure (Fig. 4). The indicator of the rolling down angle increases on its length not so sharply as in the first case. The last stage of abrasive deterioration involves flake peeling of the composition because of weakening of the layer by cracks and formation of a direct contact of the test liquid with the substrate.

Obviously, this kind of composite destruction is predetermined by two disadvantages of the systems studied. The first of them is insufficient ability of the polymer matrix of relaxation of internal stresses, which is manifested in the formation of cracks in the process of abrasive wear. The second disadvantage consists in the absence of a mechanism for secure fixing nanoscale particles on the smooth surfaces of the coarse microsize fraction. These problems can be solved in further studies using matrices with increased elasticity and fillers with a structured surface.

In general, the results of this work can be used to create a theoretical framework, which will enable design of scaleable technologies for obtaining superhydrophobic coatings. Such coatings are characterized by high manufacturability, namely the possibility of one-stage application, which is traditional in the technology of paint and varnish materials. However, in order to obtain a complete theoretical approach, additional studies are necessary to determine influence of the particle shape in the structure-forming elements and the mechanical indicators of the matrix concerning stability of the material under wear conditions.

7. Conclusions

1. It has been established that the value of critical concentration of the polymer matrix in three-fraction composite coatings is largely determined by the content of the nanoscale fraction. For a composite with 5 % by weight of this component, it is 13.0 % by weight and 19.5 % by weight for a composite with 15 % by weight. Critical concentration determines formation of a maximum wetting angle of superhydrophobic coating. For the first and second fractional composition, it was 144 and 148 degrees, respectively.
2. It was shown that when ground calcite is used as micro-size fractions, its particles form densely packed structures on the coating surface. The coarse fraction acts as a frame while the fine fraction acts as a filler. The nanosize fraction in this system occopies the structure voids and does not cover the surface of coarse elements.
3. It has been determined that the coarse fraction of the microsize filler plays a decisive role in formation of abrasive wear resistance of coatings having a hierarchical structure. However, the optimum structure is ensured by its combination with a relatively fine fraction in a ratio corresponding to the principle of dense packing of particles. For such coatings, wear resistance is 15–20 % higher than for those containing only a coarse fraction.
4. It has been shown that upon contact with abrasive particles, destruction of the hierarchical structures with the studied compositions proceeds in two stages. In the first stage, the nanoscale fraction is carried-over from the surface which is reflected in increase in the angle of water rolling down from the coating within 20 degrees. The second stage consists in formation and gradual growth of cracks in the coating structure. This ultimately leads to the exfoliation of the film composite from the substrate.

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